ontario hydro
research division

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if
Reproduced in Whole or in Part

To: Dr. D. Mills
Director of Research

A STUDY OF ONTARIO HYDRO'S CONTRIBUTION TO OZONE LEVELS IN ONTARIO: PHASE I - LITERATURE REVIEW

X. Lin
Scientist
Environmental Science Section
Chemical Research Department

ABSTRACT

The frequent occurrence of high ozone, O_3, concentrations in rural areas in southeastern Canada has become of concern to the Canadian public. Tropospheric O_3 photochemistry is discussed with special emphasis on nonlinear characteristics of O_3 production. The nonlinearity of O_3 production with respect to nitrogen oxide, NO_x levels implies that NO_x emanating from major urban centres, power plants and other industrial complexes can play an important role in regional O_3 episodes in this region. Ontario Hydro, as one of the emitters of NO_x is strongly committed to understand its contribution to the problem and to take prudent measures to reduce its impact. To help fulfil these needs, a critical review of the literature was carried out. Development of a reactive plume model, including a comprehensive photochemistry package and implementation of a state-of-the-art regional oxidant model, are proposed.

1.0 INTRODUCTION

It has been recognized for some time that elevated levels of tropospheric oxidants are responsible for crop loss, forest decline and respiratory disorders in humans (eg, Levy et al, 1977; Heck et al, 1982; Dunnett, 1983; and Skarby and Sellden, 1984). A careful statistical analysis of long-term trends based on measurements indicates that mean levels of tropospheric ozone O_3, an important oxidant, at mid-latitude in the northern hemisphere have increased by 20-100% over background values (Logan, 1985). Frequent occurrences of high O_3 concentrations in rural areas in southeastern Canada have become of concern to the Canadian public.

job	file	date	report no.
35-501-091	837.261	October 18, 1989	89-235-K

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

Ontario Hydro, as one of the emitters of nitrogen oxides, NO_x, a precursor of O_3, is strongly committed to understand its contribution to the problem of photochemical pollution and to take prudent measures to reduce its impact. A study of Ontario Hydro's contribution to O_3 levels in Ontario was therefore initiated by the Environmental Science Section of Research Division, to help address the first of these corporate interests. The ultimate aim of the study is to assess the contribution of Ontario Hydro emissions to regional photochemical oxidant episodes, and to provide firm guidelines, based on our best knowledge of the physical and chemical processes involved, for planning and implementing potentially high-cost NO_x emission reduction projects.

In the next section, a general picture of the production of tropospheric O_3 is given. This is followed by a discussion of the important nonlinear characteristics of O_3 production and their significance in regional O_3 budgets. Ontario Hydro's needs for information on this issue are then addressed. A critical review of the literature is carried out in Section 3.0. Both advantages and shortcomings of existing oxidant air quality models are discussed. Concluding remarks and a proposal for further study are presented in Section 4.0.

2.0 BACKGROUND

2.1 Photochemical Production of Tropospheric O_3

In the polluted troposphere, O_3 is generated in a nonlinear photochemical system. The O_3 precursors, NO_x and volatile organic compounds (VOCs*), are emitted into the atmosphere by both natural and anthropogenic sources. In the presence of water vapour, the hydroxyl radical is produced through the reaction of H_2O with excited atomic oxygen. The hydroxyl radical attacks VOCs and leads to the formation of organic peroxyl radicals. The peroxyl radicals then oxidize NO to NO_2, followed by photodissociation of NO_2 and production of atomic oxygen. The atomic oxygen in turn combines with molecular oxygen to form O_3. The above O_3 production route may be represented by the following highly simplified scheme

$$RH + OH + O_2 \longrightarrow RO_2 \qquad 2.1$$

$$RO_2 + NO + O_2 \longrightarrow NO_2 + HO_2 + CARB \qquad 2.2$$

$$HO_2 + NO \longrightarrow NO_2 + OH \qquad 2.3$$

$$2(NO_2 + h\upsilon + O_2 \longrightarrow NO + O_3) \qquad 2.4$$

$$\text{Net: } RH + 4O_2 + h\upsilon \longrightarrow 2O_3 + CARB \qquad 2.5$$

where RH and CARB stand for reactive hydrocarbons (ie, VOCs) and carbonyl compound, respectively. The carbonyl can go through further oxidation and produce more O_3 as well as odd hydrogen.

*The terms volatile organic compounds, VOCs, non-methane hydrocarbons, NMHC, and reactive hydrocarbons, RH, are often used interchangeably to represent the class of reactive hydrocarbons involved in the photochemical production of ozone in the troposphere.

2.2 Nonlinearity of the Tropospheric O_3 Production

The O_3 production route described by the above scheme is not simply (linearly) proportional to the levels of precursors, NO_x and VOCs. This is because the destruction rates of NO_x and odd hydrogen depend strongly on the levels of VOCs and NO_x. In addition, reactions between O_3 and alkenes, radical loss reactions of HO_2 and RO_2, and PAN formation further complicate the situation.

The nonlinear aspects of O_3 production may be investigated through a model study. A box model in which transport is highly simplified while the details of the complex photochemical processes are incorporated, as described in detail in Liu et al, (1987), Trainer et al (1987) and Lin et al (1988) can be used. A set of NO_x levels ranging from 0.1 through 100 ppbv and a set of non-methane hydrocarbon (NMHC) levels covering a domain between 1 to 1000 ppbC were specified. The model runs started at 5:00 am and continued until noon when the O_3 levels were examined relative to the specified NO_x and VOC levels. The initial level for O_3 was fixed at 30 ppbv and the mixture of VOCs was chosen as the one used by ADMP (1987) to represent regional scale distributions. The calculated O_3 is plotted against NO_x and NMHC levels in Figure 2.1. The O_3 contours show clearly a nonlinear pattern that reflects differences in photochemical behaviour between low and high levels of NO_x. When the NO_x level is below the critical level of about 0.5 ppbv, O_3 production is limited by the availability of NO_x. In this region O_3 increases with increasing NO_x and O_3 production is virtually independent of the VOC concentration. When the NO_x level is increased to 1 ppbv, the O_3 production rate no longer rises with increasing NO_x. At some higher NO_x level, the O_3 production may actually decrease with an increase in NO_x. In the region of NO_x levels above 1 ppbv, O_3 production apparently increases sharply with increasing VOC concentration.

The nonlinear behaviour shown in Figure 2.1 can be explained through an analysis of the chemical system. O_3 production is essentially limited by the reaction of VOCs with OH radicals. At low NO_x levels, the OH concentration depends on the reaction of HO_2 with NO, and increasing NO_x results in an increase of OH, hence the increase in O_3. At high NO_x levels, however, the removal mechanism for both odd hydrogen and odd nitrogen

$$OH + NO_2 \text{ ---> } HNO_3 \qquad 2.6$$

competes with the photolysis of NO_2 so that increasing NO_x tends to decrease the availability of OH. In the high NO_x regime, VOCs play a role in increasing O_3 through the competing reactions (2.1) and (2.6).

2.3 Implication of the Nonlinearity of Tropospheric O_3 Production

The results shown in Figure 2.1 have important implications in understanding regional O_3 budgets. It is seen that with NO_x below 0.5 ppbv the rate of O_3 production is small even if substantial amounts of non-methane hydrocarbons are present. Under these circumstances, observed elevated O_3 levels are due to transport from urban areas. When NO_x levels are high, say above 1 ppbv, high O_3 concentrations can develop locally with moderated amounts of anthropogenic VOCs or even smaller amounts of natural VOCs (Trainer et al, 1987).

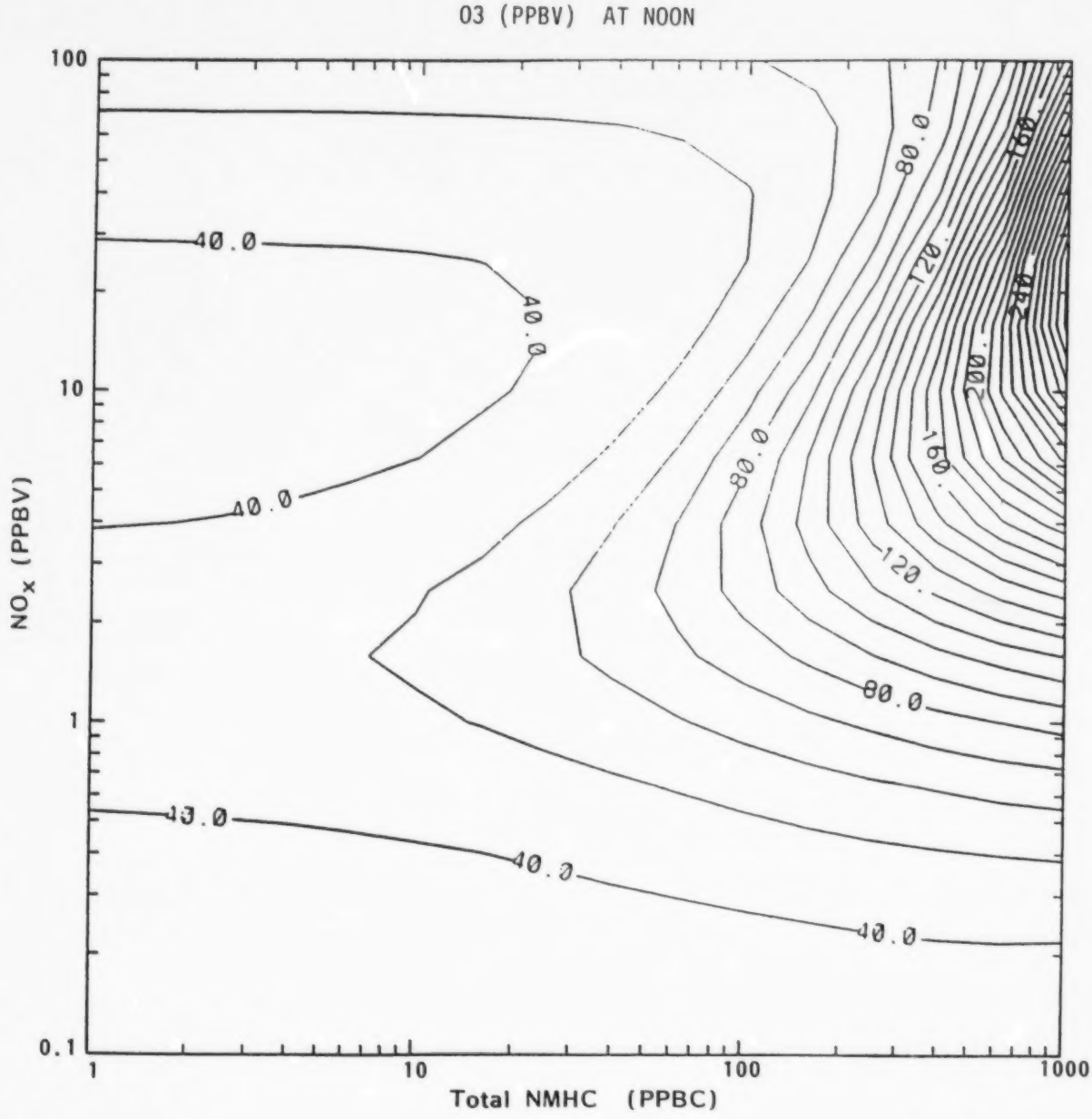

FIGURE 2.1

ISOPLETHS OF O_3 AT NOON VS. NO_x
AND TOTAL NON-METHANE HYDROCARBON LEVELS

Observations of regional NO_x reveal that typical rural values are generally above 1 ppbv in the eastern US and south-eastern Canada (Mueller and Hidy, 1982; Fahey et al, 1986 and Liu et al, 1987). Therefore, when air masses are stagnant, high O_3 levels may be generated locally as secondary pollutants accumulate. This is consistent with the observed frequent occurrence of high O_3 concentrations (>80 ppbv) on the regional scale in these areas.

However, the statement that high regional O_3 levels or O_3 episodes may develop locally does not imply that local rural emissions of the precursors are responsible. Sillman et al (1987) indicate that emission rates for NO_x must be greater than 4×10^{11} molecules/cm^2/s in order to develop an O_3 episode for a 3-day period of stagnation. Anthropogenic emissions of NO_x on a regional scale are significantly larger than natural emissions from soils, which are typically in the range of 0.2-1.3 $\times 10^{10}$ molecules/cm^2/s (Galbally and Roy, 1978; Williams et al, 1987). As pointed out by Logan (1983), in North America, fossil-fuel combustion exceeds natural sources by a factor of 3-13. Hence it is reasonable to conclude that NO_x found in rural air in the eastern US and southeastern Canada is, at least in part, transported from major urban centres, power plants and other industrial complexes.

2.4 Ontario Hydro's Concern and Needs

Plumes from fossil-fuel power stations contain significant amounts of NO_x. The NO_x is emitted mainly in the form of nitric oxide, NO. During the early stages of transport, the chemistry of nitric oxide is dominated by its reaction with O_3 which mixes into the plume from the surrounding ambient air

$$NO + O_3 \text{ ---> } NO_2 + O_2 \qquad 2.7$$

In general, this reaction is fast compared with the mixing process. Thus, the plumes are characterized by an O_3 deficit with respect to ambient levels and an increasing NO_2/NO ratio with travelling distance. Field studies (eg, Hegg et al, 1977; Melo and Stevens, 1981; Cocks et al, 1983) showed that O_3 concentrations exceeding those of the surrounding ambient air were never found in plumes which were sampled within 100 km of the stacks. However, as the plumes disperse further into the ambient atmosphere, where sufficient VOCs are available, from natural and/or anthropogenic sources, the remaining NO_x will support a significant in-situ photochemical production of O_3.

Logan (1983) indicated that the annual global NO_x production is 21×10^{12} g N/year. The value for North America is 5.8×10^{12} g N/year of which Canada contributes about 10% (United States-Canada Memorandum of Intent, 1982). The geographical distribution of NO_x emissions in North America due to the combustion of fossil fuels is presented in Figure 2.2. It is seen that, in Southern Ontario, the anthropogenic emission rates for 1980 are around 20 kg N/ha annually. According to annual reports issued by the Environmental Protection Department of Central Production Services of Ontario Hydro (see Table 2.1), the 1980 annual NO_x emissions from all of Ontario Hydro's thermal stations were about 6.6×10^{10} g which accounts for about 13% of the total anthropogenic NO_x emissions in Southern Ontario.

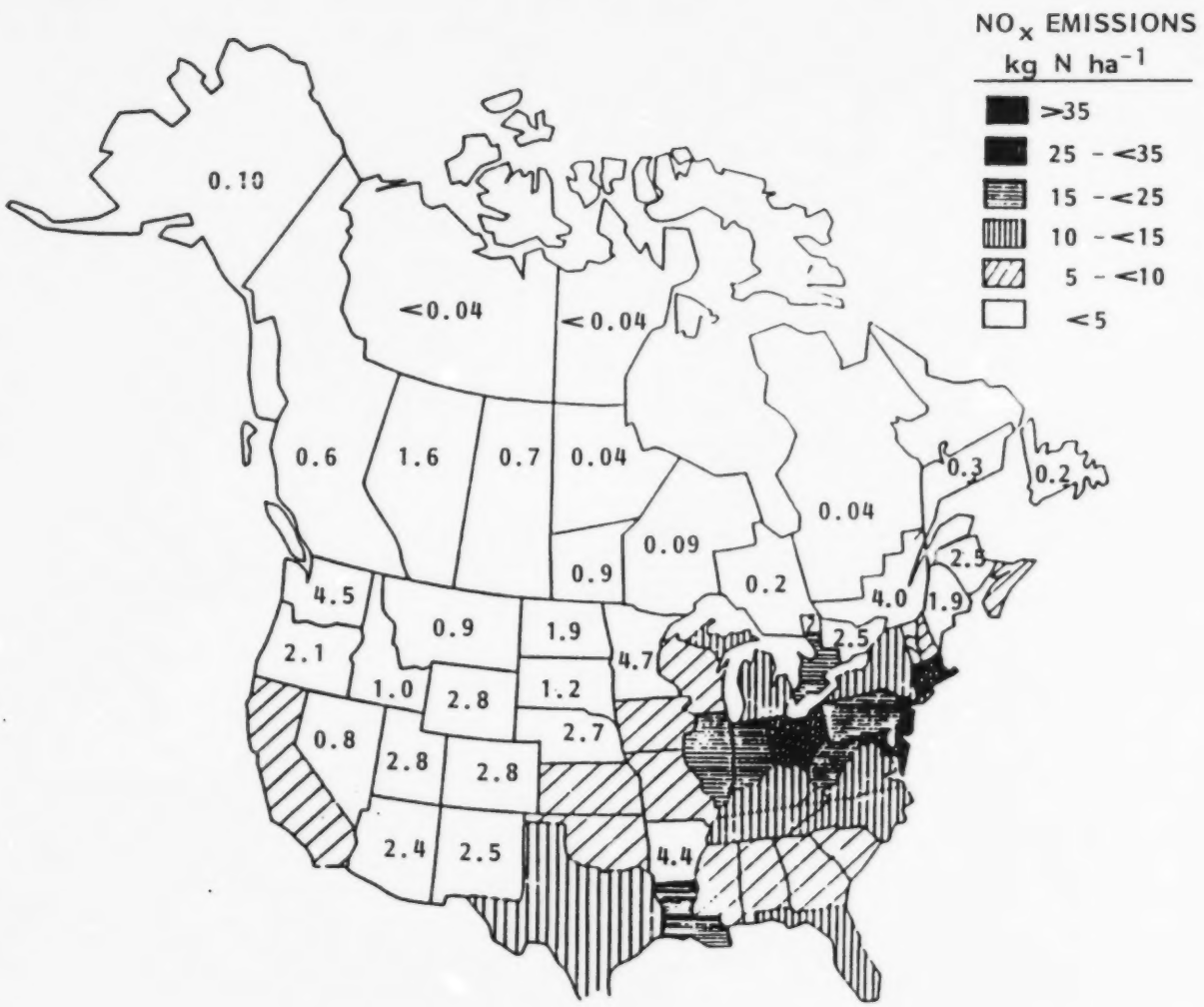

FIGURE 2.2

EMISSIONS OF NO_x IN NORTH AMERICA FROM COMBUSTION OF FOSSIL FUEL FOR 1980. AVERAGE EMISSION RATES IN EACH STATE, PROVINCE OR REGION ARE GIVEN IN UNITS OF Kg N/ha/YEAR (UNITED STATES - CANADA MEMORANDUM OF INTENT, 1982).

89-235
180962-RD

TABLE 2.1

ONTARIO HYDRO'S NITRIC OXIDE EMISSIONS DURING 1980-1988, Mg

	1980	1981	1982	1983	1984	1985	1986	1987	1988
J.C. Keith	140	690	1,400	220	200	*	*	*	*
Thunder Bay	1,010	2,100	3,800	2,800	2,400	1,400	1,800	3,200	2,900
R.L. Hearn	3,040	1,000	1,100	110	**	**	**	**	**
Lakeview	12,900	12,000	13,000	13,000	12,000	8,900	5,200	9,300	11,000
Lambton	12.300	13,000	13,000	12,000	13,000	12,000	9,900	12,000	12,000
Nanticoke	36,300	42,000	48,000	49,000	47,000	39,000	33,000	36,000	32,000
Lennox	66	190	240	***	***	***	***	47	550
Atikokan	****	****	****	****	****	290	500	1,100	1,800
TOTALS	65,756	70,980	80,540	77,130	74,600	61,590	50,400	61,647	60,250

Ontario Hydro, as one of the NO_x emitters, is interested in understanding the role of its NO_x emissions in the formation of oxidants in Ontario. An obvious question is how much Ontario Hydro contributes to high O_3 concentrations (or O_3 episodes) on regional scales in south-eastern Canada. The question deliberately excludes concerns over short-range contributions, say within a 100-km radius of the thermal stations, for the reason stated earlier. Obviously, Ontario Hydro would benefit from an answer in order to design and implement an appropriate control program. To answer the question, however, is not a trivial matter. It requires determining source-receptor relations for the region of interest.

Due to the strong involvement of nonlinear photochemistry in atmospheric transport, it would be difficult to determine the source-receptor relations from monitoring networks. The com- monly recognized approach to the problem is numerical modelling. As long as a model has been validated, the model can be used as a numerical surrogate of the real world, involving comprehensive physical and chemical processes, to identify contributions of a specified source to a specified receptor for any given period of time for which all necessary meteorological conditions and emission rates are known.

In order to design and/or implement a model for use within Ontario Hydro, a critical review of the literature was carried out. The results are given in the next section.

3.0 REVIEW OF EXISTING AIR QUALITY MODELS

Air quality models are mathematical descriptions of the atmospheric transport and/or chemical transformation of air pollutants. They operate on input data characterizing meteorology, topography and emissions over a geographical region and generate outputs describing the air quality, including information on oxidants, over the region.

Air quality models can be classified as prognostic, those that give the time evolution of the pollutants, or diagnostic, those that are only statistical descriptions of data collected over long periods. Also, air quality models can be classified as photochemical or non-photochemical (eg, pure Gaussian dispersion model). For the current interests of Ontario Hydro the present review will deal only with those models which are prognostic and involve photochemistry.

3.1 Box Models

Box models are the simplest of the numerical models. The principle to the box model concept is the assumption that pollutants in a "box" are homogeneously and instantaneously mixed. The box is bounded by the ground at the bottom, the inversion base at the top, and east-west and north-south on the sides. Primary pollutants are emitted and/or transported into the box. The ventilation or dilution is represented by the change in the upper boundary (Schere and Demerjian, 1978; Liu et al, 1987). The size of the box varies depending on the particular application of the model. In a stagnant high pressure system the box may be extended a few hundred kilometres in width.

A specific box model recommended by the US EPA for air quality control is the one frequently called EKMA (Empirical Kinetic Modelling Approach) model (Dodge, 1977a; Dodge, 1977b; Dimitriades and Dodge, 1983). The model predicts daily peak O_3 from inputs of

(1) Morning concentrations of VOCs and NO_x;

(2) Emissions of the VOCs, NO_x and other species occurring during the day;

(3) Meteorological conditions, including change rate of mixing layer height;

(4) Reactivity of VOC mixture.

The EKMA model and any box model can contain the most detailed chemical mechanism and at the same time retain computational simplicity (ie, low cost). Therefore, it is well suited to assess the effect of primary precursors on the levels of secondary pollutants. However, because of the basic assumptions mentioned above, box models can predict, at best, only the temporal variation of regionally averaged concentrations of pollutants. Due to the lack of spatial resolution they cannot be used in circumstances where meteorological conditions and emissions vary significantly across the region being modelled.

3.2 Eulerian Grid Models

Eulerian grid models employ a fixed reference coordinate system with respect to the earth to describe temporal and three-dimension spatial variations of atmospheric species (eg, McRae et al, 1981; Lamb, R.G., 1982; Carmichael and Peters, 1984; Liu et al, 1984; Pudykiewicz et al, 1985; Chang et al, 1987 and Venkatram et al, 1988). The modelled space is divided into three-dimensional grids. Horizontal dimensions of the grid cells range from tens of kilometres to a few hundreds of kilometres, while vertical dimensions vary depending on the numbers of vertical layers. Some models assume only a single well-mixed cell extending from the ground to the inversion base (eg, Sillman et al, 1987). The three-dimensional models provide the most realistic (to the best of our current knowledge) description of atmospheric physical processes including advection, diffusion, convection, cloud microphysics and deposition, affecting the transport and transformation of chemical species. The large memory requirement and huge computational burden in various complex sub-modules prohibits modellers from incorporating as much detailed chemistry as they may want.

There are inherent problems associated with a Eulerian modelling framework. One commonly recognized difficulty is the so-called "numerical diffusion" encountered in calculating advective transport. It might be overcome by adopting proper computational methods. In addition, Eulerian models, as currently designed, are not capable of resolving pollutant concentrations at the microscale, that is, at scales smaller than the size of the grid, say a few kilometres in the horizontal plan. Thus, some important local effects, eg, O_3 titration by NO near a fossil-fuel power station and very high levels of pollutants in the immediate vicinity of a large point source, tend to be obscured. To overcome the problem, the concept of nested grid submodels has existed for some time. The idea is to imbed a fine mesh grid with a coarse mesh grid to reduce the grid size in the area with large emission sources and/or large variability in concentrations. Nevertheless, no nested photochemical grid models are available at the present time.

Eulerian grid models apparently provide the best means of predicting three-dimensional variations of pollutant distributions over a region of interest. But, there are several factors preventing more scientific-technical groups from being involved in the development and application of these models. Firstly, the numerous physical and chemical sub-modules and the integration of processes with different time scales scattered from milli-seconds to years all require an interdisciplinary expert team. Secondly, a huge amount of meteorological and emission data need to be assembled as input. Finally, model runs are limited by computer resources.

In some early versions of Eulerian models, only the lowest 2-3 km of the troposphere was simulated by generally neglecting the vertical variation of atmospheric density and treating air mass exchange between boundary layer and the free atmosphere in a crude way. Some more detailed regional transport models considered only gas phase oxidation of SO_2 or NO_2 by OH radicals and, at best, included a diurnally, seasonally, or latitudinally varying linear oxidation rate. Several chemically sophisticated models (McRae et al, 1982; Lamb, 1982, 1983, 1985; Liu et al, 1984 and Sillman et al, 1989) have been developed to investigate the formation of photochemical oxidants. These models include trace gas emissions, detailed gas phase chemistry, transport and dry deposition, but neglect effects associated with clouds (aqueous chemistry, scavenging, and subgrid scale vertical transport of trace species) and/or operate with a coarse resolution.

The two latest developments in regional Eulerian models, the Regional Acid Deposition Model (RADM), developed by the Acid Deposition Model Project of the National Centre for Atmospheric Research (currently, of the State University of New York at Albany) (Chang, et al, 1987), and the Acid Deposition and Oxidant Model (ADOM), designed by Environmental Research and Technology, Inc in the US for the Ontario Ministry of the Environment and Environment Canada (Venkatram et al, 1988; Misra et al, 1989) are considered to be more comprehensive than previous models. Compared to previous Eulerian models, both RADM and ADOM have implemented detailed, updated treatment of physical and chemical processes. These processes can be summarized as

1. atmospheric transport,
2. diffusion and mixing,
3. gas phase chemistry,
4. aqueous phase chemistry,
5. dry deposition,
6. wet deposition, and
7. cloud physics.

Some detailed descriptions of the two models are listed in Table 3.1, together with the Regional Oxidant Model developed by the US EPA (Lamb, 1982; 1983; 1985).

TABLE 3.1

SOME DETAILED DESCRIPTION OF RADM, ADOM AND ROM

	RADM	ADOM	ROM
Model domain and grid size	Eastern US and southeastern Canada; 30 x 30 horizontal grid cells with approximate 80 km resolution, 6 vertical levels in the troposphere	Eastern North America 33 x 33 horizontal grid cells with 127 km resolution, 12 vertical levels between 0 and 10 km	Northeastern US in the NEROS study; about 1300 x 780 km^2 with approximate 20 km horizontal grid size; 3 prognostic "dynamic" layers that are free to expand and contract with time and space and 1 diagnostic surface layer are included
Meteorological field	Calculated from MM4 - A comprehensive prognostic mesoscale model (Anthes and Warner, 1978; Anthes et al, 1985)	Derived from a diagnostic module combining the CMC large-scale weather prediction model and a high-resolution boundary layer model of the MEP Company in Toronto, (Scholtz et al, 1986)	Wind observations and primitive equations are used jointly to derive an ensemble of cell-averaged meteorological fields (including cell layer heights) each member of which is a possible description of the flow that existed during the time that the observations were made. (An ensemble of concentration fields are then calculated from the ensemble of meteorological fields)
Gas phase chemistry	A condensed version of the explicit mechanism of Leone and Seinfeld (1985) and the carbon bond mechanism of Whitten et al, (1985); 77 reactions among 36 species (Stockwell, 1986)	A condensed version of the explicit mechanism (Lurmann et al, 1986); 100 reactions among 50 species; 30 of the 50 species are transported by advection	23 species/36 reaction mechanism developed by Demerjian and Schere (1979)

TABLE 3.1 (cont'd)

SOME DETAILED DESCRIPTION OF RADM, ADOM AND ROM

	RADM	ADOM	ROM
Aqueous phase chemistry	An hybrid equilibrium and kinetic box aqueous chemical model (Walcek and Taylor, 1986)	Aqueous-phase chemistry sub-module consisting of 25 reactions among 13 species	Not included
Dry deposition	Using parameterizations and values of Sheih et al (1979), Wesely and Hicks (1977), Wesely et al (1985) and Walcek et al (1986) to calculate turbulent, sublayer and surface resistances	Pleim et al, 1984	Using values of Hill and Chamberlain (1976), Sheih et al (1979) and Wesely (1981) to determine deposition resistances; using the expression from Sheih et al (1979) to compute deposition velocity of each species
Wet scavenging	Computed by integrating the product of the grid-average of precipitation and mean cloud water composition during each cloud lifetime (Chang et al, 1987)	Using a 1-D steady-state model (Karamchandani et al, 1986) for stratiform cloud. Using a parameterization (Warner, 1970) for cumulus cloud	Not included

3.3 Lagrangian Models

Lagrangian models are very frequently called trajectory models. They utilize a moving coordinate system associated with a mean horizontal wind to describe horizontal transport of pollutants. Since a plume originating from either an industrial or an urban emission source is moving with the meteorological wind field, Lagrangian models are also called plume models. Plume models with chemical reactions included are usually named reactive plume models.

Reactive plume models may be classified according to a variety of different criteria. Earlier studies have indicated that mixing processes existing between ambient air and the plume mass play an important role in determining oxidant concentrations, particularly O_3 (Hegg et al, 1977; Cocks et al, 1983). In general, models with complex chemistry tend to simplify the effects of the mixing processes. On the other hand, the most realistic and sophisticated representations of mixing are generally combined with relatively simple reaction schemes involving only the NO-NO_2-O_3 photochemical system. The following classification of representative reactive plume models is based on the way they treat the mixing processes.

3.3.1 Class 1 - Homogeneously Mixed Plume Models

These models treat a plume as a uniform box in which all constituents are instantaneously well mixed with their counterparts entrained from ambient air. Examples of the models are Liu et a, (1985), McRae et al (1982), Forney and Giz (1981), Cocks and Fletcher (1979, 1982, 1983), Cocks et al, 1983; Varey et al (1978) and Isaksen et al (1978). The assumption of instantaneous mixing throughout the whole plume volume implies that the rate of mixing in the plume is faster than the rates of reaction involved in the chemical system. Obviously, the assumption and the resulting lack of spatial resolution with these models is not satisfied in general. Therefore, usage of these kinds of plume models is limited.

3.3.2 Class 2 - Partially Well Mixed Plume Models

In these models it is assumed that the cross wind section of an expanding plume can be divided in expanding boxes. Within each of the boxes, homogeneously mixed fields for species are imposed. Shapes of the cross-wind section of the sub-volumes can be either rectangular (Stewart and Liu, 1981; Seigneur et al, 1983; Hov and Isaksen, 1981, Clark and Cocks, 1986) or concentric elliptical rings (Lusis, 1976; Melo et al, 1978).

The model of Stewart and Liu (1981), adopted later on by Seigneur et al (1983) in an urban air quality model, used an array of well-mixed rectangular cross sections perpendicular to the plume centreline. The sub-volumes were expanded according to prescribed dispersion parameters. A carbon-bond mechanism (Whitten et al, 1980) was incorporated into the model to treat photochemical reactions involving VOCs and oxides of nitrogen. The model was applied to the Widows Creek Power Plant in Alabama and the Oak Creek Power Plant in Wisconsin. Probably, the most apparent limitation of the model is its inability to resolve vertical plume profiles, other than Gaussian ones. Similarly, the models proposed by Hov and Isaksen (1981) and Clark and Cocks (1986) assumed either explicitly or implicitly that the plumes were well mixed in the vertical direction. This assumption is only justifiable during daytime with strong convection conditions.

A concentric elliptical ring model (Lusis, 1976; Melo et al, 1978) was developed for the NO-NO_2-O_3 system. The model was based on the ring structure concept proposed in a study of plume SO_2 oxidation by Freiberg (1976). But, unlike in Freiberg's work, the model considered reactive species (O_3) entrained into the plume from the ambient air and allowed turbulent exchanges between adjacent rings. Results from model runs showed fairly good agreement with field measurements taken in the plumes of the Nanticoke thermal station in November 1975. Nevertheless, it is worthy of note that the ring structure in the vertical direction may not be appropriate in the case of an unstable boundary layer which frequently occurs during the summer.

Although certain limitations were present, these models resolved the cross-wind profiles of mean concentration fields and were a step beyond the perfectly mixed single-box plume models.

3.3.3 Class 3 - Turbulent Kinetic Plume Models

The models discussed in the previous sub-section (3.3.2) take into account mixing processes and resolve gradients of mean concentration fields. The mixing processes, however, are physically due to dynamical turbulent effects. As deviations from an ensemble-mean concentration are present, turbulent kinetic effects emerge for any species involved in second order chemical reaction. The turbulent kinetic effect stems from a turbulent kinetic term $\langle A'B' \rangle$, where $\langle\ \rangle$ represents ensemble-means, the primes denote deviations, and A and B are concentrations of two species. The turbulent kinetic term arises mathematically from the chemical production/loss in the continuity equation for a species participating in a bimolecular reaction.

Competition between the sub-macroscale mixing rate and the reaction rate determines the relative significance of the turbulent kinetic term in controlling species variations. Some studies (eg, Donaldson and Hilst, 1972; Pitts et al, 1976) showed that, for atmospheric chemistry, the NO_x-O_3 system is sensitive to the turbulent kinetic effects.

Several studies have been devoted to incorporating the turbulent kinetic effect into the plume models. In an early study (Donaldson and Hilst, 1972), a uniformly mixed atmospheric volume was employed to quantitatively show the importance of the fine scale fluctuations on nonlinear atmospheric chemistry. Similarly, Lamb (1976), Shu (1976) and Shu et al (1976) considered an NO source within a background environment containing O_3 and took an averaging procedure on the species continuity equations over cross-sections of the plume volumes.

Kewley (1978) adapted an approach originally used in combustion modelling to account for both mean field gradients and fine turbulent kinetic effect of the plumes. Georgopoulos and Seinfeld (1986a) developed a turbulent reacting plume model in a more proper manner. In their model, including the NO-NO_2-O_3 system, all fine scale mixing effects were incorporated in the chemical kinetic terms by using a special chemical closure scheme. The modelled results quantitatively predicted the retardation on the evolution of nonlinear plume chemistry by incomplete mixing at fine scales. They showed that neglecting turbulent concentration fluctuations for NO + O_3 reactions leads to inaccuracies in plume chemistry simulation close to the source, but the oxidation rate is correctly computed at a sufficiently far downwind distance (Georgopoulos and Seinfeld, 1986b). Therefore, they do not feel it is critical to incorporate the treatment in a reactive plume model. This will be even more instructive when the chemical sub-module becomes more sophisticated.

4.0 CONCLUDING REMARKS - PROPOSAL FOR FURTHER STUDY

In the previous sections we have addressed Ontario Hydro's needs to respond to the growing environmental concern with photo-oxidant pollution and have reviewed currently available air quality models. To accommodate Ontario Hydro's needs, ie, to assess Ontario Hydro's contributions to the Canadian or Ontario's O_3 burden, we recommend that oxidant modelling simulations covering plume travelling distances of up to about 1000 km be carried out. To do this, a regional oxidant model will be invoked. In addition, a sub-grid reactive plume model will be needed since regional O_3 episodes are likely to exhibit interesting behaviour on intermediate scales, not resolved by the Eulerian models. It has been reported that oxidation of plume material may be limited by dispersion at distances of at least 650 km (Cocks et al, 1983). Due to the limited resources of the Environmental Science Section of Ontario Hydro Research, it is not practical to develop a state-of-the-art regional model internally within a reasonably short period of time. Thus, an outside model must be introduced, possibly through

collaboration with others. The development of a reactive plume model is within the Section's capability and should be pursued. The following phases of the oxidant study are proposed.

4.1 Phase 2 - Design and Test of a Comprehensive Photochemical Module

An explicit, comprehensive photochemical module which has been applied to rural areas in both the eastern and western US (Liu et al, 1987; Trainer et al, 1987 and Lin et al, 1988) will be subjected to comparisons against measurements made during the 1988 Canadian Atmospheric Chemistry Study in the Muskoka area. Some adjustments (mainly in computational techniques) may be needed to reflect the relations between primary precursors and secondary pollutants observed in the area.

4.2 Phase 3 - Development of a Reactive Plume Model

The foregoing chemical module will be integrated into a two-dimensional framework moving with the plume trajectories to form a reactive plume model. The model will account for

(1) concentration profiles in both horizontal and vertical directions on cross-wind sections of the plumes for all stability conditions;

(2) time-dependent mixing processes between the plume and the ambient environment; and

(3) emissions along the plume trajectories.

4.3 Phase 4 - Selection, Modification and Application of a Eulerian Grid Model

The Acidic Deposition and Oxidant Model (ADOM), one of the two state-of-the-art regional models in North America, will likely be selected as the regional oxidant model to fulfil Ontario Hydro's needs. The tentative selection is based on

(1) accessibility (it is easy to access via the Ontario Ministry of the Environment); and

(2) model geographical coverage (with southern Ontario at the centre of the model domain, ADOM has more Canadian coverage than RADM, see Figures 4.1 and 4.2).

In order to apply this model to the task at hand, modifications will be required in order to resolve sub-grid scale processes. This may involve the use of a reactive plume model for industrial or urban sources or the use of nested grid models.

Approved by:

for D.J.R. Dodd
Manager
Chemical Research Department

Prepared by:

X. Lin
Scientist
Environmental Science Section

Reviewed by:

O.T. Melo
Section Head
Environmental Science Section

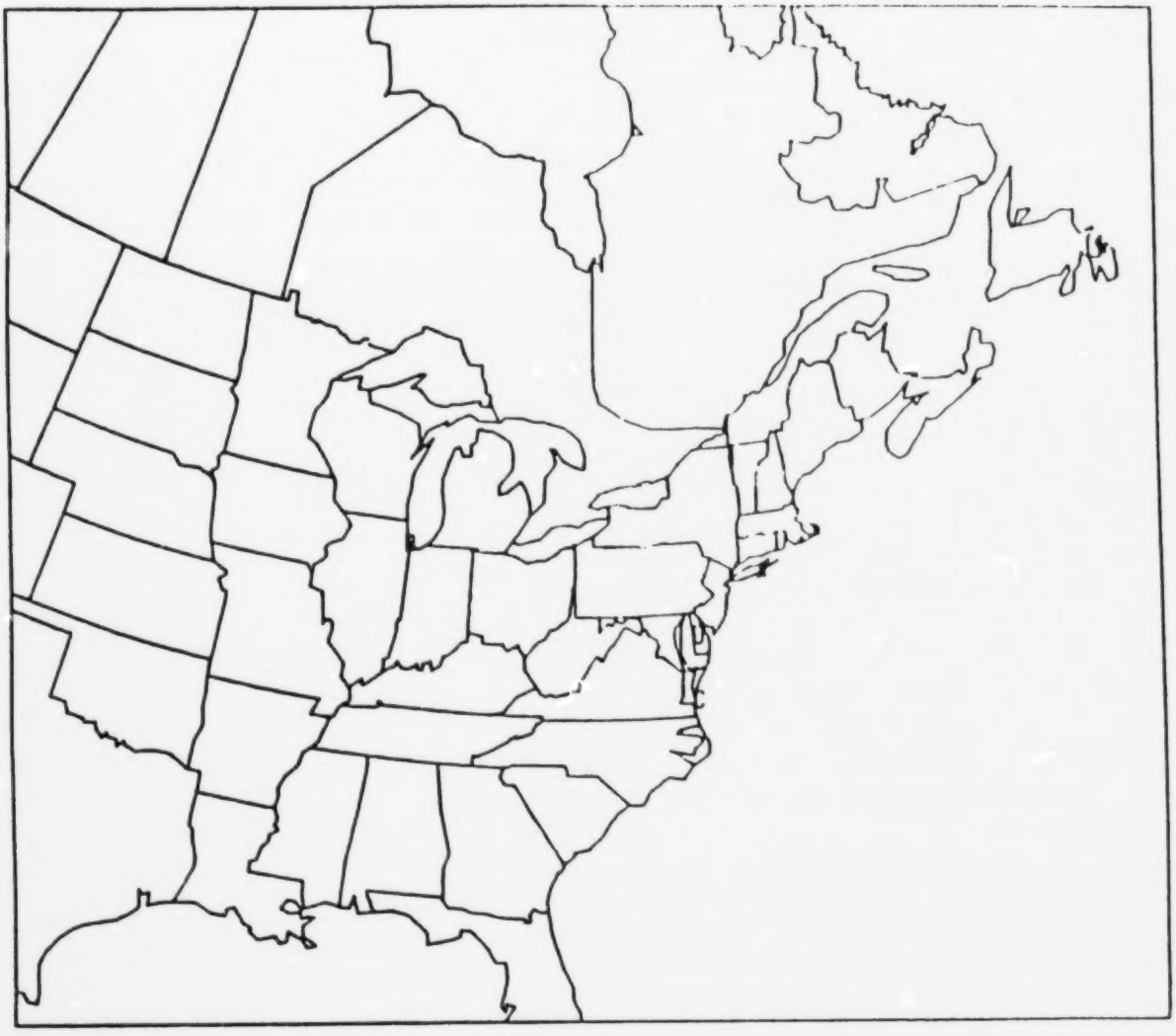

FIGURE 4.1
MODEL DOMAIN OF ADOM

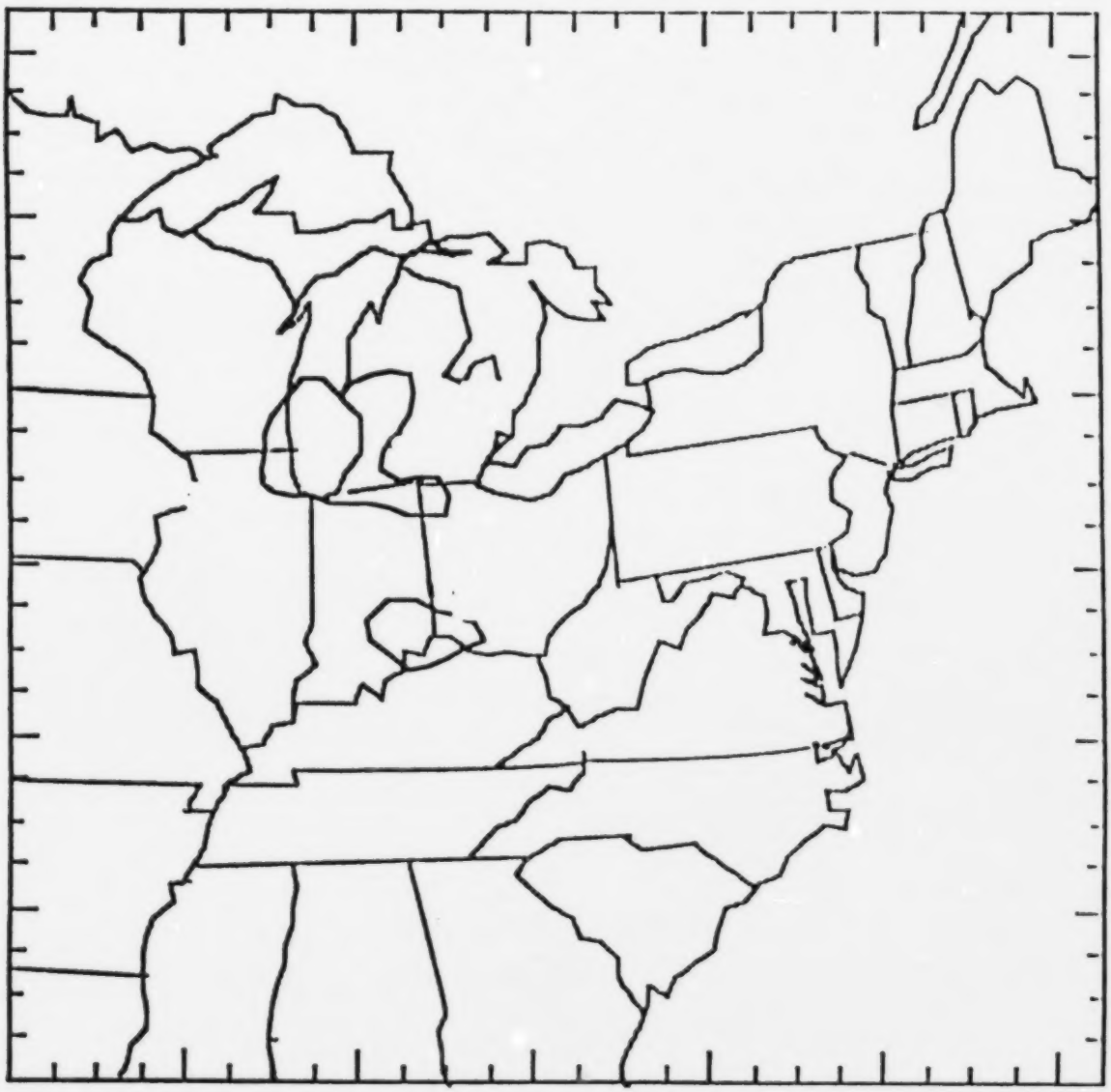

FIGURE 4.2
MODEL DOMAIN OF RADM

REFERENCES

ADMP (Acid Deposition Modeling Project), Development and implementation of chemical mechanisms for the regional acid deposition model (RADM), Report to U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1987.

Anthes, R.A., and T.T. Warner, Development of hydrodynamic models suitable for air pollution and other mesometeorological studies, Mon. Weather Rev., 106, 1045-1078, 1978.

Anthes, R.A., Y.-H. Kuo, D.P. Baumhefner, R.M. Errico and T.W. Bettge, Predictability of mesoscale atmospheric motions, Adv., Geophys., 28B, 159-202, 1985.

Carmichael, G.R., and L.K. Peters, An Eulerian transport/transformation/removal model for SO_2 and Sulfate, I, Model development, Atmos. Environ., 18, 937-951, 1984.

Chang, J.S., R.A. Brost, I.S.A. Isaksen, S. Madronich, P. Middleton, W.R. Stockwell, and C.J. Walcek, A three-dimensional Eulerian acid deposition model: physical concepts and formulation, J. Geophy. Res., 92, 14681-14700, 1987.

Clark, P.A., and A.T. Cocks, Mixing models for the simulation of plume interactions with ambient air, CERL Report No. TPRD/L/2921/N85, 1986.

Cocks, A.T., and I.S. Fletcher, Possible effects of dispersion on the chemistry of gaseous power plant effluents, Atmos. Environ., 16, 667, 1982.

Cocks, A.T., and I.S. Fletcher, A modelling study of the gas phase chemistry of power plant effluents under conditions relevant to long range transport, CERL Report No. TPRD/L/2603/R83, 1983.

Cocks, A.T., I.S. Fletcher, and A.S. Kallend, Chemical Modelling studies of the long-range dispersion of power-plant plumes, in "Air Pollution Modelling and its Applications II", Ed., C. Wispaleaere, pp. 137-157, Plenum, New York, 1983.

Demerzian, K.L. and K.L. Schere, Applications of a photochemical box model for ozone air quality in Houston, Texas, proceedings, ozone/oxidants: Interactions with the total environment II, Houston, TX, 14-17, Oct 1979, APCA, Pittsburgh, PA, pp 329-352, 1979.

Dimitriades, B. and M. Dodge, Eds., Proceedings of the Empirical Kinetic Modeling Approach (EKMA) Validation Workshop, U.S. Environmental Protection Agency Report No. EPA-60019-83-014, August, 1983.

Dodge, M.C., Combined use of modeling techniques and smog chamber data to derive ozone precursor relationship, Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control, Vol. II, Dimitriades, Ed., EPA-600013-77-001b, 881-889, 1977a.

Dodge, M.C., Effect of selected parameters on predictions of a photochemical model, U.S. Environmental Protection Agency Report No. EPA-60013-77-048, June, 1977b.

Donaldson C.P., and Hilst G.R., Effect of inhomogeneous mixing on atmospheric photochemical reactions, Eviron. Sci. Technol., 6, 812-816, 1972.

Dunnett, J.S., Ozone named as culprit, Nature, 301, 275, 1983.

Fahey, D.W., G. Hubler, D.D. Parrish, E.J. Williams, R.B. Norton, B.A. Ridley, H.B. Singh, S.C. Liu, and F.C. Fehsenfeld, Reactive nitrogen species in the troposphere: measurements of NO, NO_2, HNO_3, particulate nitrate, peroxyacetylnitrate (PAN), O_3, and total reactive odd nitrogen (NO_y) at Niwot Ridge, Colorado, J. Geophys. Res., 91, 9781-9793, 1986.

Freiberg, J., The iron-catalyzed oxidation of SO_2 to acid sulphate in dispersing plumes, Atmos. Environ., 10, 121-130, 1976.

Galbally, I.E., and C.R. Roy, Loss of fixed nitrogen from soils by nitric oxide exhalation, Nature, 275, 734-735, 1978.

Georgopoulos, P.G., and J.H. Seinfeld, Mathematical modeling of turbulent reacting plumes-I. General theory and model formulation, Atmos. Environ., 20, 1791-1807, 1986.

Georgopoulos, P.G., and J.H. Seinfeld, Mathematical modeling of turbulent reacting plumes-II. Application to the NO-NO2-O3 system, Atmos. Environ., 20, 1809-1818, 1986.

Heck, W.W., O.C. Taylor, R. Adams, G. Bingham, J. Miller, E. Preston, and L. Weinstein, Assessment of crop loss from ozone, J. Air poll. Control Assoc., 32, 353-361, 1982.

Hill, A.C. and E.M. Chamberlain, The removal of water soluble gases from the atmosphere by vegetation, Proc. Symp. on Atmosphere-Surface Exchange of Particles and Gases, ERDA Symp. Series, NTIS, p 153-170, 1976.

Hov, O., and I.S.A. Isaksen, Generation of secondary pollutants in a power plant plume: a model study, Atmos. Environ., 15, 2367-2376, 1981.

Karamchandani, P.K., F.W. Lurmann, A. Venkatram, and J.R. Young, A simplified stratiform cloud/wet chemistry module for regional modeling, Fifth Joint AMS/APCA Conference on Applications of Air Pollution Meteorology, Chapel Hill, NC, pp 110-112, 1986.

Kewley, D.J., Atmospheric dispersion of a chemically reacting plume, Atmos. Environ., 12, 1895-1900, 1978.

Lamb, R.G., Continued research in mesoscale air pollution simulation modeling: Volume III: modeling of microscale phenomena, EPA-600/4-76-016C, 1976.

Lamb, R.G., A regional scale (1000 km) model of photochemical air pollution, 1, Theoretical formulation, report, Off. of Res. and Dev., Environ. Sci. Res. Lab., U.S. Environ. Prot. Agency, Research Triangle Park, N.C., 1982.

Lamb, R.G., A regional scale (1000 km) model of photochemical air pollution, 2, Input processor network design, report, Off. of Res. and Dev., Environ. Sci. Res. Lab., U.S. Environ. Prot. Agency, Research Triangle Park, N.C., 1983.

Lamb, R.G., A regional scale (1000 km) model of photochemical air pollution, 3, Tests of numerical algorithms, report, Off. of Res. and Dev., Environ. Sci. Res. Lab., U.S. Environ. Prot. Agency, Research Triangle Park, N.C., 1985.

Leone, J.A. and J.H. Seinfeld, Comparative analysis of chemical reaction mechanisms for photochemical smog, Atmos. Environ., 19, 437-464, 1985.

Levy, D., M. Gent, and M.T. Newhouse, 1977, Relationship between acute respiratory illness and air pollution levels in an industrial city, Am. Rev. Respir. Dis., 116, 167.

Logan, J.A.,Nitrogen Oxides in the Troposphere: global and regional budgets, J. Geophys. Res., 88, 10785-10807, 1983.

Logan, J.A.,Atmospheric ozone: seasonal behavior, Trends, and anthropogenic influence, J. Geophys. Res., 90, 10463-10482, 1985.

Lin, X., M. Trainer, and S.C. Liu, On the nonlinearity of the tropospheric ozone production, J. Geophys. Res., 93, 15879-15888, 1988.

Liu. S.C., M. Trainer, F.C. Fehsenfeld, D.D. Parrish, E.J. Williams, D.W. Fahey, G. Hubler, and P.C. Murphy, Ozone production in the rural atmosphere and the implications for regional and global ozone distributions, J. Geophys. Res., 92, 4191-4207, 1987.

Liu, M.-K., R.E. Morris, and J.P. Killus, Development of a regional oxidant model and application to northeastern United States, Atmos. Environ., 18, 1145-1161, 1984.

Lurmann, F.W., A.C. Lloyd and R. Atkinson, A chemical mechanism for use in long-range transport/acid deposition computer modeling, J. Geophys. Res., 91, 10905-10936, 1986.

Lusis M.A., Mathematical modelling of chemical reactions in a plume, Proceedings of the 7th International NATO/CCMS Technical Meeting on Air Pollution Modelling and Its Application, Airlie, Virginia, 7-10, September, pp., 831-855, 1976.

McRae, G.J., W.R. Goodin, and J.H. Seinfeld, Mathematical modeling of photochemical air pollution, Rep. 18, 661 pp., Environ. Qual. Lab., Calif. Inst. of Technol., Pasadena, 1981.

Melo, O.T., M.A. Lusis, and Stevens R.D.S., Mathematical modelling dispersion and chemical reactions in a plume-oxidation of NO to NO2 in the plume of a power plant, Atmos. Environ., 12, 1231-1234, 1978.

Melo, O.T. and R.D.S. Stevens, The occurrence and nature of brown plumes in Ontario, Atmos. Environ., 15, 2521-2529, 1981

Misra, P.K., R. Bloxam, C. Fung and S. Wong, Non-linear response of wet deposition to emissions reduction: a model study, Atmos. Environ., 23, 671-687, 1989.

Mueller, P.K., and G.M. Hidy, The sulfate regional experiment: Report of findings, Rep. 1901, (3 vols.), Electric Power Research Institute, Palo Alto, CA, 1983.

Pitts, J.N., and A.M. Winer, K.R. Darnell, G.J. Doyle, and J.M. McAfee, Chemical consequences of air quality standards and of control implementation programs: roles of hydrocarbons, oxides of nitrogen and aged smog in the production of photochemical oxidant, Final Report to the California Air Resources Board under Contract No. 4-214 by Statewide Air Pollution Research Center, University of California, Riverside, 1976.

Plein, J., A. Venkatram, and R. Yamartino, ADOM/TADAP model development program, Volume 4: The dry deposition module, ERT document No. P-B980-520, 1984.

Pudykiewicz, J., R. Benoit, and A. Staniforth, Preliminary results from a partial LRTAP model based on an existing meteorological forecast model, Atmos. Ocean., 23, 267-303, 1985.

Schere, K.L. and K.L. Demerjian, A photochemical box Model for urban air quality simulation, Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants, American Chemical Society, Washington, DC, 1978.

Scholtz, M.T., B. Weisman, L. Mahrt and A.D. Christie, Generation of meteorological data fields for the ADOM Eulerian regional model, Fifth Joint AMS/APCA Conference on Applications of Air Pollution Meteorology, Chapel Hill, NC, pp 145-150, 1986.

Seigneur, C.,T.W. Tesche, P.M. Roth, and M.K. Liu, On the treatment of point source emissions in urban air quality modeling, Atmos. Environ., 17, 1655-1676, 1983.

Sheih, C.M., Application of a statistical trajectory model to the simulation of sulfur pollution over the northeastern United States, Atmos. Environm. 11, 173-178, 1977.

Sheih, C.M., M.L. Wesely and B.B. Hicks, Estimated dry deposition velocities of sulfur over the eastern United States and surrounding regions, Atmos. Environ. 13, 1361-1368, 1979.

Shu, W.R., Turbulent chemical reactions: applications to atmospheric chemistry, Ph.D. thesis, Department of Chemical Engineering, California Institute of Technology, 1976.

Shu, W.R., R.G. Lamb, and J.H. Seinfeld, A model of second-order chemical reactions in a turbulent fluid-II. Applications to atmospheric plumes, Atmos. Environ., 12, 1699-1705, 1976.

Sillman, S., D.J. Jacob, J.A. Logan, C.M. Spivakovsky, R.M. Yevich, and S.C. Wofsy, Theoretical Studies of long range Transport of Oxidants, final report, Coordinating Research Council, Project No. AP-9, 1987.

Skarby, L., and G. Sellden, The effects of ozone on crops and forests, Ambio, 3, 68-72, 1984.

Stewart, D.A., and M.K. Liu, Development and application of a reactive plume model, Atmos. Environ., 15, 2377-2393, 1981.

Stockwell, W.R., A homogeneous gas phase mechanism for use in a regional acid deposition model, Atmos. Environ., 20, 1615-1632, 1986.

Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H. H. Westberg, F.S. Fehsenfeld, and S.C. Liu, Models and observations of the impact of natural hydrocarbons on rural ozone, Nature, 329, 705-707, 1987.

United States-Canada Memorandum of Intent on Transboundary Air Pollution, Work Group 3B, Engineering Costs and Emissions, Final Report, June 1982.

Venkatram, A., P.K. Karamchandani, and P.K. Misra., Testing a comprehensive acid deposition model, Atmos. Environ., 22, 737-747, 1988.

Walcek, C.J., and G.R. Taylor, A theoretical method for computing vertical distributions of acidity and sulfate production within growing cumulus clouds, J. Atmos. Sci. 43, 339-355, 1986.

Walcek, C.J., R.A. Brost, J.S. Chang, and M.L. Wesely, SO_2 , sulfate and HNO_3 deposition velocities computed using regional landuse and meteorological data, Atmos. Environ., 20, 949-964, 1986.

Warner, J., On steady state one-dimensional models of cumulus convection, J. Atmos. Sci., 27, 1035-1040, 1970.

Wesely, M.L., and B.B. Hicks, Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation, J. Air Pollut. Control Assoc., 27, 1110-1116, 1977.

Wesely, M.L., D.R. Cook, R.L. Hart and R.E. Speer, Measurements and parameterization of particulate sulfur dry-deposition over grass, J. Geophys. Res., 90, 2131-2143, 1985.

Whitten G.Z., H. Hogo, and J.P. Killus, The carbon-bond mechanism: a condensed kinetic mechanism for photochemical smog, Environ. Sci. Technol, 14, 690, 1980.

Whitten, G.Z., P.K. Linnus, and R.G. Johnson, Modeling of auto exhaust for smog chamber data for EKMA development, U.S. Environmental Protection Agency Report, Contract 68-02-3735, Sys. Appl. Inc., San Rafael, Calif., 1985.

Williams, E.J., D.D. Parrish, and F.C. Fehsenfeld, Determination of nitrogen oxide emissions from soils: results from a grassland site in Colorado, United States, J. Geophys. Res., 91, 2173-2180, 1987.